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13. ABSTRACT (Maximum 200 words)

The long-term objective of this research is to develop structure-property relationships for the diffusion of associating and solvating penetrants in polymers, which can be used to guide the selection or synthesis of polymers for use as protective barriers or separation membranes. The immediate objective of this project was to understand, using FTIR-ATR spectroscopy, how penetrant-penetrant and penetrant-polymer interactions, particularly hydrogen bonding, dictate transport rates through polymers using model experimental systems and appropriate transport models There were three specific goals for this project: (1) determine transport mechanisms for associating penetrants in polymers; (2) determine transport mechanisms for penetrants that solvate with groups in the polymer; and (3) determine transport mechanisms in polymers for two penetrants capable of solvation with each other. Respectively, the systems studied to achieve each specific goal were: (1) acetic acid in polyisobutylene; (2)methyl ethyl ketone in vinyl alcohol/vinyl butyral copolymers, and acetonitrile and deuterated hexane, separately, in H_{12}MDI polyurethanes; and (3) mixtures of methyl ethyl ketone and butanol in polyisobutylene. In each case, the spectroscopic technique was able to identify the actual diffusing species and elucidate the mechanisms of diffusion at the molecular level.

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Molecular Transport Mechanisms for Associating and Solvating Penetrant in Polymers

Final Progress Report
1 December 1999 to 30 March 2003

Statement of Problem Studied

The long-term objective of this research is to develop structure-property relationships for the diffusion of associating and solvating penetrants in polymers, which can be used to guide the selection or synthesis of polymers for use as protective barriers or separation membranes. The immediate objective of this project was to understand how penetrant-penetrant and penetrant-polymer interactions, particularly hydrogen bonding, dictate transport rates through polymers using model experimental systems and appropriate transport models.

There were three specific goals for this project:

(1) Determine transport mechanisms for associating penetrants in polymers, both above and below the glass transition temperature.
(2) Determine transport mechanisms for penetrants that solvate with groups in the polymer.
(3) Determine transport mechanisms in polymers for two penetrants capable of solvation with each other.

Summary of Results

1. Transport mechanisms for associating penetrants in polymers, above and below the glass transition temperature.

Time-resolved Fourier Transform Infrared, Attenuated Total Reflectance (FTIR-ATR) spectroscopy was used to characterize the diffusion of acetic acid in polyisobutylene (PIB) at different vapor activities in order to understand complex diffusion mechanisms and probe molecular structures above the glass tranisition. The relationship between the carbonyl (C=O) stretch at 1715 cm^{-1}, which represents a cyclic dimer, and an unknown structure at 1726 cm^{-1} was investigated during the diffusion process to determine the structure of the unknown species. A local equilibrium association model suggested that the unknown species was a linear dimer in equilibrium with the cyclic dimer. A mathematical model for diffusion with isomerization, assuming local equilibrium, predicted that each species would have the same effective diffusion coefficient, but the individual diffusion coefficients could not be separated from the expression for the effective diffusion coefficient. Numerical simulations of the two coupled continuity equations were performed to show that the individual diffusion coefficients can be separated and that they are equal to each other for the acetic acid/PIB system. The values of the individual diffusion coefficients are consistent with the structural hypothesis from the local equilibrium assumption.

Transport of an associating penetrant below the glass transition temperature proved elusive as reproducibility in the model system, methanol in polycarbonate, was problematic. Poor adhesion between the polymer and the ATR crystal was the largest hurdle. A number of

alternative polymers were considered, including polynorbornene, polysulfone, and polyetherimide, but adhesion to the ATR crystal was poor in these systems as well. However, this problem is not insurmountable as the PI and collaborators at the University of Bologna have studied swelling in glassy polymers using FTIR-ATR spectroscopy with some success (M. Giacinti Baschetti, E. Piccinini, T. A. Barbari, and G. C. Sarti, "Diffusion of Small Molecules in Polymers: Quantitative Analysis of Polymer Swelling During Sorption Using ATR-FTIR Spectroscopy", submitted to *Macromolecules*).

<u>2. Transport mechanisms for penetrants that solvate with groups in the polymer.</u>

The diffusion of methyl ethyl ketone (MEK) in two vinyl alcohol/vinyl butyral (VA/VBu) copolymers (11- and 19-wt % VA) was studied at low vapor activities using Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy. MEK has the ability to interact through hydrogen bonding to sites in the polymer, and was chosen to study the effect of penetrant-polymer solvation on molecular diffusion. The assumption of local equilibrium was verified by examining the time-evolved concentrations of hydrogen-bound and free MEK determined from the carbonyl (C=O) stretching bands. A mathematical model was developed to account explicitly for solvation during the diffusion process. Solvation hindered the diffusion of MEK in the VA/VBu copolymer by factors of 2.0 (11-wt % VA) and 2.6 (19-wt % VA). After separating solvation from diffusion, the true diffusion coefficients of MEK were compared to the diffusion coefficients of methylene chloride (CH_2Cl_2), a non-interacting penetrant of similar size to MEK. Within experimental error, the true diffusion coefficients for MEK were the same as those for CH_2Cl_2 over the concentration range studied.

The diffusion of deuterated hexane in conformational isomers of the aliphatic polyurethane, H_{12}MDI (4,4'-dicyclohexylmethane diisocyanate) / BD (1,4-butanediol) / PTMO (poly (tetramethylene oxide)), was investigated at a fixed hard segment content of 29.9 wt% and compared to the diffusion of acetonitrile. The effective diffusion coefficient of acetonitrile, measured previously by our group, decreased with increasing trans-trans isomer content while that for deuterated hexane remained constant with changing isomer content. These results suggest that the trend observed for acetonitrile diffusion is a function of penetrant-polymer interactions and not tortuosity effects. A model with penetrant-polymer binding to the surface of the dispersed hard segment domains of the heterogeneous polymer was developed to elucidate the main factors contributing to the interaction or hindrance effects, which were determined to be the "available" surface binding sites and the surface to volume ratio of the hard segment domains. FTIR-ATR spectroscopy was used to quantify this interaction effect and SAXS was used to confirm the findings.

<u>3. Transport mechanisms in polymers for two penetrants capable of solvation with each other.</u>

The diffusion of methyl ethyl ketone (MEK)/1-butanol (BOH) mixtures in polyisobutylene (PIB) was studied at varying mixture compositions. Diffusion coefficients and hydrogen bonding interactions were quantitatively measured using the spectroscopic technique. In the MEK/BOH/PIB system, three species were identified from the infrared spectra, free MEK, an MEK-BOH complex, and a self-associated BOH cluster. The diffusion coefficient for the MEK-BOH complex was less than that for free MEK but larger than the values determined for the BOH cluster. These results were compared to a numerical solution of a multicomponent transport model that explicitly accounts for penetrant-penetrant interactions to determine

individual diffusion coefficients for all the species identified. In addition, the MEK/BOH/PIB results were compared to those for an MEK/acetonitrile (ACN) mixture, a non-hydrogen bonding system, in PIB, to elucidate the differences between interacting and non-interacting systems. After accounting for the concentration dependence, the free MEK diffusion coefficient from the interacting system compared well to that for MEK in the non-interacting system. If gravimetric or permeation techniques were used to measure MEK diffusion coefficients in both systems, the value in the interacting system would have been lower owing to hydrogen bonding with BOH, which hinders the transport of a fraction of the MEK molecules.

Diffusion of a Series of Ketones in PIB

In addition to the original project objectives, the diffusion coefficients for a series of ketones (acetone, MEK, and 2-pentanone) were measured at 40^{o}C in PIB as a function of penetrant activity and then extrapolated to infinite dilution to examine the effect of molecular size on diffusion. The values at infinite dilution were correlated with the size parameter, critical volume, using a power law relationship. The scaling exponent was determine to be –1.9, a value that is comparable to other rubbery polymers, such as poly(dimethyl siloxane), which has a scaling exponent of –2.2. The same power law relationship, when applied to diffusion coefficients at equal thermodynamic activity, resulted in exponents ranging from 2.1 to 2.3, suggesting that size effects can be determined from data at finite concentrations. Since many polymers are not amenable to study by inverse gas chromatography, the common method of measuring infinite dilution diffusion coefficients, and extrapolation of data at finite concentrations can lead to errors, the results at equal thermodynamic activity suggest a convenient method to obtain size effects for penetrant diffusion in polymers. Glassy polymers have much higher values for this scaling exponent, such as –8 or –9. Although PIB has diffusion coefficients on the same order of magnitude as glassy polymers (and comparable free volumes), it is unable to discriminate on the basis of molecular size, much like a rubbery polymer.

List of papers submitted or published under ARO sponsorship during the project

Papers published in peer-reviewed journals:

Y. A. Elabd and T. A. Barbari, "Acetic Acid Diffusion in Polyisobutylene: Probing Small Molecule Structures", *Ind. Eng. Chem. Res.*, 40, 3076-3084 (2001).

Y. A. Elabd and T. A. Barbari, "Separating Solvation from Molecular Diffusion in Polymers", *AIChE J.*, 47, 1255-1262 (2001).

Y. A. Elabd, J. M. Sloan, N. Beck-Tan, and T. A. Barbari, "The Effect of Penetrant-Polymer Interactions on Diffusion in Conformational Isomers of a Heterogeneous Polymer", *Macromolecules*, 34, 6268-6273 (2001).

Y. A. Elabd and T. A. Barbari, "Multicomponent Diffusion of Hydrogen Bonding Solutes in a Polymer", *AIChE J.* 48, 1610-1620 (2002).

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Papers published in non-peer reviewed journals or conference proceedings:

None

Papers presented at meetings, but not published in conference proceedings:

Y. A. Elabd and T. A. Barbari, “Acetic Acid Diffusion in Polyisobutylene: Probing Small Molecule Structures”, 1999 Annual Meeting of the American Institute of Chemical Engineers, November 1, 1999.

T. A. Barbari and Y. A. Elabd, “Understanding the Role of Penetrant-Polymer Solvation on Small Molecule Diffusion”, 1999 Annual Meeting of the American Institute of Chemical Engineers, November 2, 1999.

Y. A. Elabd and T. A. Barbari, “Probing Complex Molecular Transport Mechanisms with FTIR-ATR Spectroscopy”, 1999 Annual Meeting of the American Institute of Chemical Engineers, November 2, 1999.

Y. A. Elabd and T. A. Barbari, “Diffusion with Solvation in Homogeneous and Heterogeneous Polymeric Membranes”, 11th Annual Meeting of the North American Membrane Society, May 25, 2000.

Y. A. Elabd and T. A. Barbari, “Multicomponent Diffusion of Interacting Penetrants in Polymer Membranes,” Gordon Research Conference - Membranes: Materials and Processes, New London, CT, July 2000.

Y. A. Elabd and T. A. Barbari, “Small Molecule Transport Mechanisms in Polymers: Insights from FTIR-ATR Spectroscopy”, Third Joint China/USA Chemical Engineering Conference, Beijing, China, September 28, 2000.

Y. A. Elabd and T. A. Barbari, “Multicomponent Diffusion of Interacting Penetrants in a Polymer”, 2000 Annual Meeting of the American Institute of Chemical Engineers, November 13, 2000.

Y. A. Elabd, J. M. Sloan, N. Beck Tan, and T. A. Barbari, “Diffusion in a Phase-Segregated Polymer with Reversible Binding to Dispersed-Phase Surfaces,” 2000 Annual Meeting of the American Institute of Chemical Engineers, November 15, 2000.

Y. A. Elabd and T. A. Barbari, “Understanding Multicomponent Transport in a Polymer Membrane for the Separation of Interacting Mixtures”, Spring 2001 National Meeting of the American Chemical Society, April 5, 2001.

T. A. Barbari, “Membrane Transport Models Using the Chemical Theory of Solutions”, 2002 Annual Meeting of the American Institute of Chemical Engineers, November 4, 2002.

T. A. Barbari, “Membrane Transport Models Based on the "Chemical" Theory of

Solutions", Gordon Research Conference (invited), Membranes: Materials & Processes, August 5, 2002.

T. A. Barbari and C.-H. Huang, "Diffusive Size Selectivity in a Low Free Volume Rubbery Polymer", Spring 2003 National Meeting of the American Chemical Society, March 25, 2003.

Manuscripts submitted, but not published:

C.-H. Huang and T. A. Barbari, "Diffusion of a Series of Ketones in Polyisobutylene: Effect of Molecular Size", *Polymer* (in preparation).

Technical Reports:

None

Scientific Personnel Supported on this Grant

Principal Investigator:	Dr. Timothy A. Barbari
Graduate Students:	Yossef Elabd (Ph.D. Johns Hopkins University, 2000)
	Fred Huang (M.S. University of Maryland, 2001)
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Inventions

None